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CONVENIENT ONE-POT SYNTHESIS OF ARENESULFINAMIDES: REACTIONS OF 4-NITROPHENYL SUBSTITUTED PHENYL SULFOXIDES WITH ELEMENTAL SULFUR IN LIQUID AMMONIA

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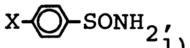
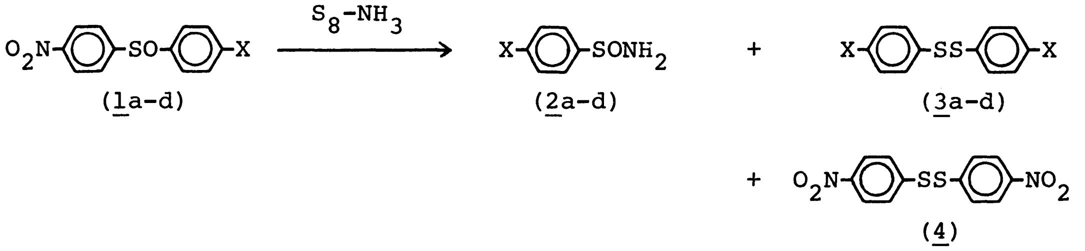
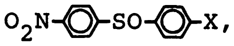
Various arenesulfinamides were synthesized in good yields by one-pot reactions of 4-nitrophenyl substituted phenyl sulfoxides with elemental sulfur in liquid ammonia. The arenesulfinamides were further reduced with elemental sulfur in liquid ammonia to give corresponding disulfides.

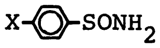
Arenesulfinamides, , are usually prepared by the reactions of arenesulfinyl halides with amines.[1) This preparation is, however, limitted in the point of yields. The alkylations of N-sulfinylaniline with Grignard reagent were also reported by H. Gilmann and K. Klamann respectively, giving N-alkyl arenesulfinamides.[2) Recently D. N. Harpp et al. reported the oxidation of arenesulfenyl N-phthalimide and subsequent exchange of amines affording N-alkyl arenesulfinamides.[3) On the other hand, direct conversion of arenesulfinic acid to arenesulfinamides with pyridinium salt was also reported by M. Furukawa et al..[4) Moreover, M. Haake reported the formation of N,N-dialkyl arenesulfinamides by the reactions of N,N-dialkyl arenesulfenamides with N-chlorosuccinimide in methylene chloride and subsequent hydrolysis with aq. $KHCO_3$.[5) Thus, there have been only five types of synthetic methods of the arenesulfinamides. These methods are, however, very complex and the overall yields of resulting arenesulfinamides are relatively low. In the course of our investigations on the reactions of organosulfur compounds with elemental sulfur in liquid ammonia,[6,7) we studied a new synthesis of arenesulfinamides. We now report a convenient one-pot synthesis of arenesulfinamides from 4-nitrophenyl substituted phenyl sulfoxides with elemental sulfur in liquid ammonia at ambient temperature (eq.1).



(1a-d) (2a-d) (3a-d) (4) (eq.1)

Substrates, 4-nitrophenyl substituted phenyl sulfoxides(1a-d), were prepared

Table 1. Reactions of 4-Nitrophenyl Substituted Phenyl Sulfoxides,  with Elemental Sulfur in Liquid Ammonia$^{a)}$

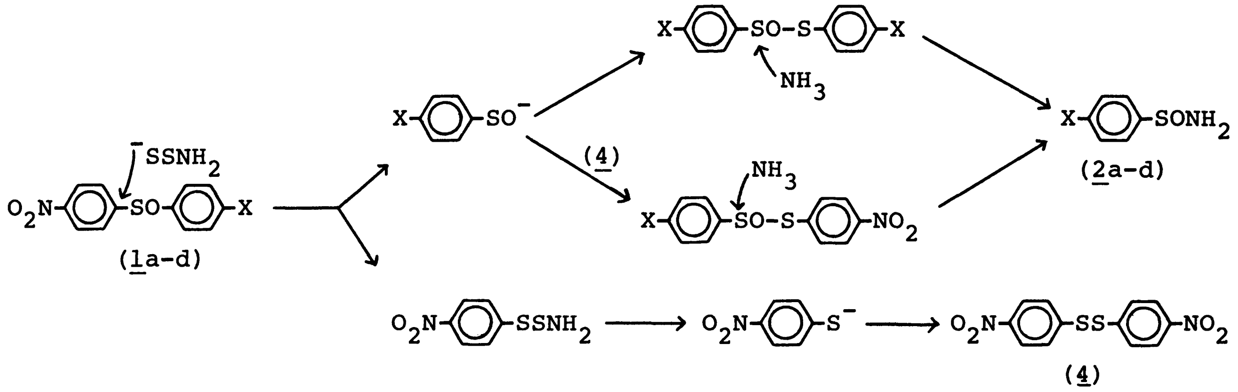
Run	Substituent X		React Temp (°C)	React Time(h)	S_8 (mg atom)	Yield of Sulfinamides(%) 
1	CH_3	1a	20	2	2	65
2	CH_3	1a	20	6	2	66
3	CH_3	1a	60	2	2	49
4	CH_3	1a	80	2	2	8
5	CH_3	1a	20	2	1	43
6	CH_3	1a	20	2	3	57
7	Cl	1b	20	6	2	65
8	H	1c	60	2	2	58
9	NO_2	1d	20	2	2	38
10$^{b)}$	CH_3	1a	20	2	0	trace

a) Substrate: 1 mmol, Liquid Ammonia: 10 ml,

b) Benzenethiol (2 mmol) was added.

by the reactions of arenethiols with 4-chloronitrobenzene in liquid ammonia and subsequent oxidation with hydrogen peroxide in acetic acid. In this reaction, products are arenesulfinamides(2a-d), diaryl disulfides(3a-d) and 4,4'-dinitrodiphenyl disulfide(4). Typical procedure is as follows. 4-Nitrophenyl substituted phenyl sulfoxide and elemental sulfur were taken into all titanium autoclave. After evacuation liquid ammonia is charged into the autoclave. Reaction mixtures were separated by column chromatography on silica gel(Wako gel C-300) using chloroform as eluent. The obtained sulfinamides(2a-d) were identified by NMR, Mass, IR and elemental analysis. Results of this reaction are summarized in Table 1.

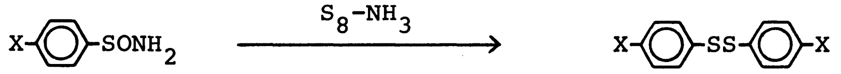
The results in Table 1 show that various arenesulfinamides are obtained in good yields by one-pot reactions of 4-nitrophenyl substituted phenyl sulfoxide with elemental sulfur in liquid ammonia at low temperature such as 20°C. (Run 2,7, 8 and 9) When benzenethiol instead of elemental sulfur was used in this reaction, desired sulfinamide was obtained only in trace(run 10). This fact suggests that the elemental sulfur in liquid ammonia plays an important role in this reaction. We have already reported the formation of ammonium aminothiolate or aminodithiolate, $H_2NS^-NH_4^+$ or $H_2NSS^-NH_4^+$, and its nucleophilic reactions toward 4-chloronitrobenzene$^{8)}$ and benzylchloride$^{9)}$ to give sulfides. In the present reaction, aminothiolate apparently attacks on 1-arylcarbon of 4-nitrophenyl ring at initial stage to leave ammonium arenesulfenate. Recently we have reported the reactions of 4-nitrophenyl aryl and alkyl sulfones with elemental sulfur in liquid ammonia to yield aryl$^{7)}$ and alkyl$^{10)}$ thiosulfonic acids. These reactions were also illustrated by the initial attack of aminothiolate on 1-arylcarbon of 4-nitrophenyl ring. Sulfenic acid is well known to disproportionate to thiolsulfinate.$^{11)}$ The formation of arenesulfinamides can be interpreted by



Scheme 1.

the nucleophilic attack of ammonia on sulfinyl sulfur of the thiolsulfinate. However, since the high yields of the sulfinamides(run 2) cannot be explained by only above mechanism, another path is necessary to consider. Another path is an attack of arenesulfenate anion on sulfenyl sulfur in 4,4'-dinitrodiphenyl disulfide(4), which is formed from 4-nitrobenzenethiosulfenamide, O_2N-⌬-$SSNH_2$, with elemental sulfur in liquid ammonia,[12] affording 4-nitrophenyl benzenethiolsulfinate, O_2N-⌬-S-SO-⌬-X, and then nucleophilic attack of ammonia on sulfinyl sulfur of the thiolsulfinate giving arenesulfinamide and 4-nitrobenzene thiolate. These are depicted in Scheme 1.

Surprisingly, in the reactions at high temperature such as 80°C and 100°C the yield of arenesulfinamide decreased. The yields of sulfinamides were low in the cases of the reactions for long time and using 3 mg atom of elemental sulfur. These results suggest that the sulfinamides resulted further react with elemental sulfur in liquid ammonia(eq.2). To confirm these reactions



(2a-d) (3a-d) (eq. 2)

we carried out the reactions of arenesulfinamides with elemental sulfur in liquid ammonia and found the reduction of arenesulfinamides to corresponding diaryl

Table 2. Reactions of Arenesulfinamides with Elemental Sulfur in Liquid Ammonia[a)]

Run	Sulfinamide	React.	S_8	Yield of product(%)	
	X-⌬-$SONH_2$	Temp (°C)	(mg atom)	X-⌬-SS-⌬-X	
1	CH_3-⌬-$SONH_2$	60	2	CH_3-⌬-SS-⌬-CH_3	32
2		80	2		62
3		100	2		76
4		100	3		83
5		100	1		41
6	⌬-$SONH_2$	100	3	⌬-SS-⌬	89
7		100	2		79
8		100	1		44

a) Substrate: 1 mmol , Liquid Ammonia: 10 ml , Reaction Time: 4 h , disulfides in good yields. These results are summarized in Table 2.

Thus the arenesulfinamides were reduced with elemental sulfur in liquid ammonia at high temperature such as 100°C affording diaryl disulfides (run 3, 4, and 6). Accordingly, the low yields of run 4 and 6 in Table 1 are interpreted by the reaction of arenesulfinamides with elemental sulfur in liquid ammonia. We have already reported the reduction with elemental sulfur in liquid ammonia, e.g. the reduction of nitrogen functional groups.[13, 14] Above results suggest that the reaction system of elemental sulfur in liquid ammonia is very useful for the reduction of not only nitrogen functional groups but also sulfur functional groups.

Thus arenesulfinamides were synthesized in good yields and were further reduced to corresponding diaryl disulfides with elemental sulfur in liquid ammonia. These reactions are also very important as conversion of arenethiols to arenesulfinamides with elemental sulfur in liquid ammonia. The applications for synthetic chemistry of elemental sulfur in liquid ammonia are now in progress.

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